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Impact of non-polar solvents in dynamic nuclear polarization at high magnetic fields

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Keywords: Dynamic nuclear polarization Hyperpolarization in liquids High frequency microwave propagation Electron spin relaxation Organic radicals	Dynamic nuclear polarization (DNP) in liquids can enhance NMR signals by up to two orders of magnitude at magnetic fields greater than 9.4 T. The DNP experiment relies on driving electron spin transitions through microwave irradiation of the sample, which requires the solvent/sample to be transparent to microwaves. The physical models describing spin polarization transfer neglect the role of the solvent, despite recent experimental results suggesting that its impact on DNP efficiency can be as much as a factor of three. In this study, we aim to clarify how and why the solvent may affect DNP experiments at high magnetic fields. We examined known systems (¹³ C-CCl ₄ /TEMPO and PPh ₃ /BDPA) dispersed in CCl ₄ , heptane, and benzene. By measuring their EPR properties, simulating microwave propagation patterns, and quantitatively assessing the DNP enhancements at 14.1 T, we determined that the choice of non-polar solvent is not critical to the outcome of a DNP experiment. Furthermore, our experimental results and electromagnetic simulations enable us to assess the state-of-the-art capabilities of DNP instruments at high magnetic fields and propose directions for possible future improvements.			

Dynamic Nuclear Polarization (DNP) is a technique used to enhance nuclear magnetic resonance (NMR) signals by transferring spin polarization from highly polarized electron spins to nearby nuclear spins. In most DNP applications, organic radicals carry unpaired electron spins, while the target nuclear spins are located on nearby molecules [1]. The spin polarization transfer is driven by microwave (MW) irradiation on resonance with the electron spin transitions, and in the liquid state, it relies on electron-nuclear cross-relaxation via either Overhauser effect (OE) [2–5] or Solid Effect (SE) [6,7]. The enhanced nuclear polarization improves the sensitivity of NMR experiments, allowing for better detection and characterization of molecules in solutions.

At high magnetic fields ($B \ge 3$ T), achieving efficient DNP can be challenging due to (*i*) inefficient relaxation dynamics [5,8] and (*ii*) the need for high-power MW sources, such as gyrotrons, to effectively saturate the electron spin transition.

Recently, it has been shown that ${}^{13}C$ [9–13], ${}^{19}F$ [12,14], ${}^{31}P$ [15,16], and also ${}^{1}H$ [6,7] can be efficiently hyperpolarized at 9.4 T and above. These results provide exciting prospects for the application of

DNP-enhanced NMR spectroscopy on a large variety of compounds. The experiments are typically conducted on mixtures of an organic radical (or polarizing agent, PA), a target molecule of interest, and a solvent, usually chosen for its favorable dielectric properties, which help reduce the MW absorption and heating. Furthermore, low solvent viscosity favors the spin polarization transfer when it is dominated via electronnuclear dipolar coupling [17], while there is no indication the solvent has a role when the scalar coupling dominates [18,19]. Recent experimental observations have shown that scalar-dominated ³¹P enhancements in triphenylphosphine (PPh₃) at very low magnetic fields (1.2 T) can vary by a factor of up to ~10 depending on the solvent used [20]. This finding suggests that the solvent could significantly impact the outcome of a DNP experiment, having a role either as a mediator or participant in spin polarization transfer mechanisms, or affecting the relaxation properties of the system.

Liquids have notoriously high MW absorption coefficients especially at high frequencies (>100 GHz) [21], therefore the efficient implementation of DNP experiments is heavily influenced by the dielectric

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properties of the solvents and requires careful management of experimental conditions to optimize signal gains. As MW travels though the liquid, the absorbed energy limits the MW propagation, and dissipates as heat rather than contributing to the DNP process, leading to reduced polarization efficiency, inhomogeneous DNP enhancement, nonuniform temperature distributions in the sample, and possibly sample boil-off. This makes accurate quantitative DNP experiments at high magnetic fields particularly challenging. Various experimental approaches have been proposed to mitigate heating effects while maximizing the MW magnetic field $(B_{1,MW})$. The use of MW cavities, small sample volumes (less than 100 nL), and high power gyrotrons, pioneered by Griffin's [22] and Prisner's [23,24] groups, allows to achieve $B_{1,MW}$ high enough to fully saturate the electron transitions and give NMR enhancements up to ~400 at 9.4 T [10]. A second approach, based on non-resonant probes, allows for large sample volumes (\sim 10–30 µL) but it is limited to non-polar solvents [13,15,16]. More recently, Bennati et al. [12] introduced a DNP-NMR probe that combines thin sample layers and efficient MW beam shaping to significantly reduce heat losses in sample volumes up to 20 µL, leading to enhancements up to 120, and previously unmatched NMR resolution under MW irradiation (~0.02 ppm on ¹³C linewidth).

In this study, we aim to clarify the solvent's role in DNP experiments at high magnetic fields. We investigated two well-studied target molecule/radical systems from recent DNP literature, i.e. 13 C-CCl₄/TEMPO and PPh₃/BDPA, both of which exhibit high enhancements at high magnetic fields thanks to the large hyperfine coupling between the unpaired electron and target nuclei [9,20]. These compounds were dispersed in the solvents CCl₄, heptane, and benzene (Fig. 1) and we systematically characterized their EPR properties (linewidth, correlation time τ_c), MW absorption, sample heating, and DNP enhancements at 14.1 T. Our results reveal that within the class of non-polar solvents, the specific choice of solvent neither significantly affects the DNP enhancement nor the spin polarization transfer at high magnetic fields. Finally, our work provides insight into key aspects of microwave (MW) propagation in liquids at high magnetic fields, indicates the current



Fig. 1. Schematic of the samples prepared for this work by dissolving a polarizing agent (TEMPO or BDPA) and a target molecule (CCl_4 or PPh_3) in a non-polar solvent (CCl_4 , benzene, or heptane).

performance of state-of-the-art liquid DNP instruments, and evaluates the limitations and potential directions for future advancements.

1. Experimental methods

1.1. Sample preparation

Solvents (tetrachloromethane CCl₄, benzene C₆H₆, heptane C₇H₁₆), radicals ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl – TEMPO, 1,3-bisdiphenylene-2-phenylallyl – BDPA), and target molecules (¹³C-CCl₄, triphenylphosphane – PPh₃) were purchased from Millipore Sigma and used as received. Samples for both EPR and DNP-NMR measurements were degassed with at least four freeze-pump-thaw cycles, and transferred to a sample tube in an argon glove-box. The samples were either transferred in a FEP (fluorinated ethylene propylene) tube and sealed by welding, or in a quartz tube, sealed with an air-tight cap.

1.2. Continuous-wave EPR

Continuous-wave EPR was performed at four frequencies, 9 GHz, 240 GHz, 316 (or 336) GHz, and 395 GHz. Measurements at 9 GHz were performed on a benchtop Bruker EMX Nano. Measurements at 240 GHz and 316 (or 336) GHz were performed on a quasi-optical heterodyne EPR spectrometer [25,26], while a transmission spectrometer was used to record spectra at 395 GHz [41]. In all cases, the modulation amplitude was below 0.1 mT and the sweep rate was set to 0.08 mT/s or lower. To minimize the magnetic field inhomogeneity both from the static magnetic field and from the modulating field, we used a small sample volume (15 µL), sealed in an FEP tube. The sample volume occupies a cylinder 2 mm in diameter and 5 mm in height, which is within the homogeneity region of the magnet (15 ppm over 1 cm along the z-axis of the magnet). Data analysis to fit the spectra and extract the full-width half-maximum (FWHM) was performed with an in-house software [25, 26]. To obtain the correlation time from the CW-EPR spectra, we used the simulation package Easyspin (6.0.6) [27,28].

1.3. CST Studio simulations

The MW propagation patterns were simulated with finite-element simulations with CST Studio suite 2024 (Dassault Systemes). The 3D models of the terminal part of the horn antenna, the sample tube, and the solvent were drawn with Autodesk Inventor (Autodesk). In the electromagnetic simulations, all conductors were approximated to ideal conductors. The dielectric properties of materials and solvents (CCl₄, benzene, hexane, toluene) reported here were measured in the range 370–420 GHz with a method described in Ref. [29].

1.4. Dynamic nuclear polarization measurements

DNP-enhanced NMR experiments were performed on a DNP instrument consisting of a 14.1 T Oxford magnet, Tecmag Redstone NMR console, and a Bruker-CPI second-harmonic 395 GHz gyrotron as a highpower MW source [16]. The MW beam power and polarization is manipulated with a quasi-optical bench, which also houses a shutter to rapidly switch the MW irradiation on and off. The MW power estimated at the sample position is ~10–15 W [16,30]. The probe is a home-build triple-resonance ¹H/X/e probe based on a Varian HX 600 MHz [13,16]. The probe is equipped with a set of two sweep coils that allows field sweeps of ± 20 mT around the central field position. Prior to MW irradiation, the sample was cooled to ~-13 °C with cold nitrogen gas that flows inside the waveguide and along the sample walls.

2. Results and discussion

2.1. EPR

The EPR spectra of TEMPO radical in solutions were recorded in CCl₄, benzene, and heptane, which are some of the most popular nonpolar solvents used in DNP. We probed four concentrations: 0.1, 1, 5, 10 mM, where the highest concentrations are typical for DNP experiments. Fig. 2 shows the spectra at a 10 mM TEMPO radical concentration, while spectra recorded at lower concentrations are shown in the Supplementary Information. The spectra show three lines, each corresponding to one spin packet in the nitrogen manifold. Each line is inhomogeneously broadened by the proton isotropic hyperfine coupling [31,32], and can be fitted with good agreement to purely Lorentzian lines (Fig. 2). At 10 mM radical concentration, the average line width ΔB_{avg} , calculated as the arithmetic average of the line widths of the three lines ΔB_i (*i* = 1,2,3), is affected by inhomogeneous broadening due to electron-electron dipolar coupling. At 9 GHz, ΔB_{avg} is solvent dependent, ranging from 0.37 mT for CCl₄ to 0.95 mT for heptane; at 395 GHz, which corresponds to the irradiation frequency of our DNP instruments at 14.1 T, $\Delta B_{avg} \sim 0.9$ mT independently of the solvent.

At lower concentrations, the dipolar coupling is much reduced. and If there are no inhomogeneity effects due to the static magnetic field, the measured linewidth should approach the intrinsic width due exclusively to hyperfine coupling to ¹H nuclei and tumbling dynamics. To verify that, we simulated EPR spectra using the hyperfine couplings reported in the literature [42] without any additional convolutional broadening (Fig. 3). At 9 GHz, the experimental spectrum recorded for 0.1 mM radical concentration shows additional homogeneous broadening compared to the simulated spectrum. In contrast, at 395 GHz, the lines broaden homogeneously due to rotational dynamics and are well reproduced by the simulation. (Fig. 3). Therefore, the value of $\Delta B_{avg} \sim 0.43 \pm 0.03$ mT at 395 GHz is close to the minimum achievable at magnetic fields relevant for DNP applications.

From the line width ΔB_{avg} , we determined $T_{2,e}$, with the following equation which applies in the case of purely Lorentzian lines:

$$T_{2,e} = \frac{1}{\pi \cdot \Delta \nu_{avg}},\tag{1}$$

where $\Delta \nu_{avg} = \gamma_e \cdot \Delta B_{avg}$, with $\gamma_e = 28.036$ MHz/T as the electron gyromagnetic ratio.

Fig. 4 shows $T_{2,e}$ values as a function of frequency for different solvents and radical concentrations. $T_{2,e}$ exhibits a frequency dependence, decreasing from approximately $T_{2,e} \sim 30-50$ ns at 9 GHz to $T_{2,e} \sim$



Fig. 3. CW EPR spectra recorded at 9 GHz and 395 GHz on a sample of TEMPO (0.1 mM) dissolved in CCl₄. The right panel is a zoom in on the central line. The simulations were performed in the fast motion regime (Easyspin, routine *garlic*), without convolutional or inhomogeneous broadening and taking into account 18 protons, twelve with $A_{iso} = 0.64$ MHz, four with $A_{iso} = 1.09$ MHz, two with $A_{iso} = 0.5$ MHz [42]. The individual lines are visible at 9 GHz but not at 395 GHz due to the homogeneous broadening. Correlation time was set at $\tau_c = 4.6$ ps as estimated from the fit of EPR spectra. Field axis are normalized to the field of the central line B_0 .

10–30 ns at 395 GHz. This trend is particularly evident for CCl₄ but is less pronounced for heptane. At the conditions at which we performed DNP (395 GHz and 10 mM radical concentration) $T_{2,e}$ is independent of the solvent and is $T_{2,e} \sim 12$ ns. At a lower radical concentration of 0.1 mM, $T_{2,e} \sim 25$ ns, limited by inhomogeneous line broadening. These values are in fairly good agreement with previously reported values of $T_{2,e} \sim 10-20$ ns for nitroxide radicals in water and organic solvents at 263 GHz [12,33]. On the contrary, rapid scan EPR measurements on deuterated TEMPONE in water in the frequency range 250 MHz–34 GHz give a flat frequency dependence with $T_{2,e} \sim T_{1,e} \sim 300$ ns [34], corresponding to a linewidth of ~0.4 G. This discrepancy arises because deuteration reduces anisotropic broadening by a factor of $\gamma_{1H}/\gamma_{2H} \sim 6.5$ compared to the protonated radical.

The rotational correlation times τ_c were extracted from the spectra at different concentrations and frequencies. The average values are reported in Table 1 and agree well with previously reported ones [34,35]. Given previous investigation on the role of the rotational correlation



Fig. 2. CW-EPR spectra recorded at 9, 240, and 395 GHz of TEMPO radical (10 mM) dispersed in (a) heptane; (b) CCl₄; (c) benzene. The solid lines are fit with Lorentzian functions. Deviations between the simulated curves and 395 GHz spectra are attributed to phase instabilities. Field axis are rescaled to the field position of the central line B_0 .



Fig. 4. Electron transverse relaxation time $T_{2,e}$ of TEMPO radical as a function of frequency obtained from CW-EPR linewidth. (**a–c**) Each panel reports $T_{2,e}$ for three solvents with radical concentration (a) 10 mM, (b) 1 mM, and (c) 0.1 mM. (**d–f**) $T_{2,e}^*$ as a function of frequency for (d) heptane; (e) CCl₄; and (f) benzene at different radical concentrations. Error is estimated as 15 %, error bars are not shown for clarity.

Table 1

Solvent viscosities at room temperature ($20^{\circ}-25^{\circ}C$) and TEMPO radical correlation times (average and standard deviation) estimated by fitting six EPR spectra collected at 240 GHz and 316 GHz for each solvent. The fit were performed with *Easyspin (chili)* [27,2,8] and purely Lorentzian line shapes.

$\eta \text{ (mPa-s)}$	$\tau_{\rm c}$ (ps)	
0.39-0.42	2.8(0.7)	
0.86-0.96	4.6(0.5)	
0.60	4.1(1.5)	
	η (mPa·s) 0.39–0.42 0.86–0.96 0.60	

time in Overhauser DNP [35,36], we expect no contribution of the radical rotation to the electron-nuclear spin polarization transfer [35].

2.2. MW irradiation profiles

The performance of DNP experiments critically depends on the homogeneous irradiation of the sample. In our DNP instrument, the samples can be accommodated in 3-mm outer diameter tubes made out of either clear fused quartz (also known as fused silica) or FEP. The sample tube is mounted on a horn antenna and irradiated from the bottom with MW beam that propagates with a TE₁₁ mode at 395 GHz (Fig. 5a). The liquid sample fills the tube to a height of 2 cm, corresponding to a volume of ~80 μ L for the quartz tube and 17 μ L for the FEP tube.

The MW propagation through the horn antenna, the sample tube, and the liquid sample was simulated as described in the Experimental section. The dielectric properties of the tube materials and of the solvents used in the simulations were measured in the range 370–420 GHz with a methodology reported in Ref. [29] and are reported in Table 2. The extinction coefficients *k* of both FEP and quartz are low $(\sim 1.15 \cdot 10^{-3} \text{ or less})$, indicating that both tubes are low-absorbing. However, the refractive index of quartz is 30 % higher (2.04 vs. 1.46), making it more likely to disrupt the MW path.

Non-polar solvents such as pentane, hexane, and CCl₄ have similar refractive indexes (between 1.40 and 1.46) but different extinction coefficients *k*, which vary between $1.07 \cdot 10^{-3}$ of pentane, the least absorbing, and $3.07 \cdot 10^{-3}$ of CCl₄. From these values one can calculate the penetration depth as $\delta_p = 1/\alpha$, where α is the extinction coefficient given by $\alpha = 4\pi k/\lambda$, where $\lambda = \lambda_0/n$ is the wavelength in the material with λ_0 the wavelength in vacuum. At 395 GHz ($\lambda_0 = 0.75$ mm) the MW penetration depth δ_p varies significantly in non-polar solvents, ranging from 4.0 cm for pentane to 1.1 cm for CCl₄. In toluene, which has a slightly polar molecule, δ_p goes down to ~0.5 cm.

The profile of the magnetic field component *B* of the MW beam (B_{1} , $_{MW}$) is shown in Fig. 5 for pentane and toluene in FEP (Fig. 5b) and quartz tube (Fig. 5c). The simulations use a linearly-polarized coherent microwave beam which gives a periodic power distribution in the sample, with visible peaks and troughs (Fig. 5b and c). In all cases, the sample tube walls provide a guide for the MW propagation, which is mostly confined within the sample volume. As expected, the different dielectric properties of the liquid largely impact the propagation profile, which looks more homogeneous and less dampened along the sample length in pentane than in toluene (Fig. 5b and c). A quantitative comparison is shown in Fig. 5d: along the 2 cm of the sample, $B_{1,MW}$ decays



Fig. 5. (a) 3D schematics of the arrangement of the horn and sample tube used in DNP experiments. (b) Longitudinal cross section and dimensions of the FEP sample tube. The maps show the magnetic field component $B_{1,MW}$ of the MW beam in pentane and toluene. (c) Longitudinal cross section and dimensions of the quartz tube, and $B_{1,MW}$ maps. In the simulations, the MW input power is 0.5 W (<0.01 W reflected by the port) and the input mode is TE₁₁. (d) $B_{1,MW}$ in the sample volume and along the tube axis. (e) Transversal cross section of the sample tube showing the contour of the MW magnetic field $B_{1,MW}$.

Table 2

Dielectric properties (*n*: refractive index, *k*: extinction coefficient; tan δ : loss tangent; α = absorption coefficient) at 395 GHz for materials and solvents utilized in this work. The values of *n* and *k* were obtained experimentally in the range 370–420 GHz with a methodology that was previously described [29]. The loss tangent was calculated as tan $\delta = 2 k/n$ and the absorption coefficient as $4\pi k/\lambda$. The penetration depth is $\delta_{\mathbf{p}} = 1/\alpha$.

Material	n	k (×10 ⁻³)	$ an\delta$ (×10 ⁻³)	α (cm ⁻¹)	$\delta_{\rm p}$ (cm)
Fused quartz	2.04	1.00	0.980	0.338	3.0
FEP	1.46	1.15	1.575	0.278	3.6
Pentane	1.40	1.07	1.529	0.248	4.0
Hexane	1.44	1.32	1.833	0.315	3.2
CCl ₄	1.46	3.70	5.068	0.895	1.1
Toluene	1.56	7.57	9.690	1.957	0.5

by ~ 12 % in pentane, while it goes down by ~ 52 % in toluene.

Comparison of MW propagation patterns reveals distinct differences between FEP and quartz tubes (Fig. 5b and c), arising from their different materials and geometries. In the FEP tube, the MW is rather homogeneous across the sample cross section, and the beam profile resembles a TE₁₁ mode with minimal distortions (Fig. 5e). On the contrary, the quartz tube produces a lens effect that focuses the MW beam in the bottom part of the sample and along the tube axis (Fig. 5b,c,e). This focusing effect results from two properties of the quartz tube: its bottom curvature and higher refractive index (n = 2.04, Table 2), as confirmed by additional simulations (Supplementary Information).

To quantitatively compare the results, we calculated $B_{1,\rm MW}$ over a MW time period ($B_{1,\rm MW}^{\rm avg}$) (Fig. 6). As a consequence of the lens effect, the maximum $B_{1,\rm MW}^{\rm avg}$ value in quartz tube is larger than in FEP (Fig. 6, top panel). However, when considering the mean across the whole sample volume, the FEP tube is better than the quartz one, with $B_{1,\rm MW}^{\rm avg}$ that is 30–50 % larger than the one in the quartz tube (Fig. 6, bottom panel). The actual excitation field that is effective in driving electron transition when irradiating with a non-coherent linearly polarized source is $B_{1,e}^{\rm avg} = B_{1,\rm MW}^{\rm avg}/\sqrt{2}$ because only half of the power of the linearly polarized beam is absorbed by the rotating spins.

2.3. DNP enhancement

DNP measurements were performed at 14.1 T, which corresponds to 150 MHz for ¹³C detection, and 395 GHz for electron resonance. The experiments monitored the ¹³C NMR signals from 500 mM of the target molecule ¹³C-CCl₄ dispersed in the solvents heptane, CCl₄, and benzene doped with TEMPO 10 mM radical. Additionally, we performed similar experiments by monitoring the ³¹P enhancements of PPh₃ doped with BDPA dissolved either in CCl₄ or benzene. The experiments were performed in both FEP and quartz tubes.



Fig. 6. Maximum (top) and mean (\pm standard deviation) (bottom) of $B_{1,MW}^{avg}$ (in mT) in the sample volume obtained from electromagnetic simulations with incident power 0.5 W.

In a DNP experiment, the enhancement is conventionally estimated by comparing the spectra with MW on (enhanced) and MW off (thermal equilibrium). However, it could be challenging to separate heating effects due to MW absorption from the effects of the spin polarization transfer, leading to an inaccurate estimation of the enhancement. In fact, under MW irradiation, even when the electron transitions are not excited (off-resonance), the NMR signal shifts and decreases in intensity (Supplementary Information). To overcome this limitation, instead of comparing MW-on and MW-off conditions, we perform DNP experiments on-resonance versus off-resonance with respect to the electron transition. This approach provides a reference signal (off-resonance) that accounts for the effects of the MW irradiation (temperature deviation and gradients due to MW absorptions) while excluding spin polarization transfer. The enhancements were calculated using the formula:

$$\varepsilon = I_{\rm on-res}/I_{\rm off-res}$$
 (2)

where $I_{\text{on-res}}$ and $I_{\text{off-res}}$ are the integrals of the signals when the MW irradiation is on-resonance and off-resonance, respectively.

Quantitative DNP experiments at 14.1 T were performed with an 8 s

gate for the MW and a repetition time of 24 s, where the MW gating limits excessive heating and sample boil-off. Under these DNP conditions, the sample temperature is 45° – 65° C, as determined by calibration with KBr [37] and by monitoring the chemical shift deviation. As expected, the enhancement profiles match the width of the EPR spectra collected at 395 GHz (Fig. 7). Although the three lines of TEMPO radical are in some cases not clearly distinguishable, the largest enhancement is obtained when the central EPR line is irradiated. The enhancement values for ¹³C-CCl₄/TEMPO and ³¹P-PPh₃/BDPA are plotted in Fig. 8a and b respectively, and reported in Table S1 and S2.

Fig. 8 shows that the enhancements are only marginally influenced by the sample tube (quartz or FEP). The differences in $B_{1,MW}^{avg}$ found with electromagnetic simulations do not convert to a significant difference in effective saturation of the electron transitions in the two cases, probably due to the limited MW power at the sample (as discussed below). Overall, the choice of solvent does not appear to be critical for maximizing the enhancements, which are, within error, very similar across different samples and solvents (Fig. 8). We notice differences between FEP tubes and quartz tubes, but we can't identify a trend. These inconsistencies could be tentatively ascribed to the different thermal conductivities of the two materials. The enhancements for PPh₃/BDPA are not solvent-dependent, which differ from what has been obtained at much lower magnetic fields (1.2 T), where enhancements for PPh₃ in



Fig. 8. NMR signal enhancements for (a) 13 C-CCl₄/TEMPO and (b) PPh₃/BDPA in different solvents and tubes.



Fig. 7. (a-d) CW-EPR spectra recorded at 395 GHz in first derivative (as recorded, bottom), absorption shape (middle), and corresponding 13 C-enhancement profiles at 14.1 T (top). The radical concentration is 10 mM for both EPR and DNP measurements. (e, f) 13 C and 31 P spectra recorded at 14.1 T under MW irradiation on resonance with the electron transition and off resonance. The lines are in homogeneously broadened by the not perfect homogeneity of the sweep coils.



Fig. 9. Maximum enhancement achievable on 13 C-CCl₄ with OE-DNP in liquids as a function of the magnetic field and calculated for different levels of electron saturation *s* (black lines). The experimental data are from the literature [9,10,12,30] and from this work (at 14.1 T).

benzene were approximately 60 % higher than those in CCl₄. From our experiments, we conclude that at high magnetic fields and in the investigated systems, the solvent does not have a significant impact in scalar-dominated spin polarization transfer.

In the final section, we discuss the limitations of the current setup and the potential for improvement. The maximum enhancement recorded for 13 C-CCl₄ is \sim 17, aligning well with previously reported values at the same field [12,30]. This enhancement represents only 10 % of the predicted ε_{max} (Fig. 9 and Supplementary Information) based on the classical description of the Overhauser effect in liquids [3,38]. This discrepancy is primarily attributed to the insufficient saturation of the electron transition, caused by several factors. First, MW irradiation is inhomogeneous across the sample volume. Based on the dependency of the electron saturation factor $s = s(B_{1,\text{MW}}^{\text{avg}}, T_{1,e}, T_{2,e})$ (Supplementary Information) [39,40], the estimated experimental $B_{1,\text{MW}}^{\text{avg}}$ in the ¹³C-CCl₄/TEMPO sample is 0.04 mT. By comparing this with the electromagnetic simulations, we deduce that despite the 12 W provided by the gyrotron source, only <3 W reaches the sample (Supplementary Information). These values could be significantly improved by reducing the sample volume and optimizing microwave delivery to the sample. Second, at 14.1 T with 10 mM radical concentration the electron $T_{2,e}$ is rather short ($T_{2,e} \sim 12$ ns): achieving a longer $T_{2,e}$ of ~ 25 ns could potentially double the electron saturation, and thus the enhancement (Supplementary Information).

3. Conclusions

In this work, we analyzed how different non-polar solvents affect the electron and nuclear magnetic resonance properties of samples prepared for DNP in liquids at high magnetic fields. We found that the EPR line width of TEMPO radicals, and thus the transverse electron relaxation time, is frequency and solvent dependent, but it converges to $T_{2,e} \sim 12$ ns at 395 GHz/14.1 T and 10 mM radical concentration (typical for DNP experiments). With electromagnetic simulations, we verified that while the MW propagation pattern is solvent dependent, it is strongly influenced by the sample tube geometry and material, with plastic being preferred over quartz. Our DNP results at 14.1 T, obtained while carefully excluding thermal effects, show that the enhancements obtained on the selected target molecules (¹³C-CCl₄ and PPh₃) diluted in heptane, CCl₄, or benzene are solvent independent. By combining the simulation results, the experimental results, and previous studies on the same molecular systems, it was possible to identify that at 14.1 T the saturation of the electron transition is limited by the delivered power, MW field inhomogeneity and sample size, and electron $T_{2,e}$. With optimal developments in probe design and the selection of radicals with longer relaxation times, we expect an increase of up to a factor of 5 in the performance of DNP in liquids at 14.1 T.

CRediT authorship contribution statement

Tomas Orlando: Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Huyen Bui:** Methodology. **Jhersie Cabigting:** Data curation. **Natalie Ibbetson:** Data curation. **Johan van Tol:** Writing – review & editing, Methodology, Data curation. **Thierry Dubroca:** Writing – review & editing, Methodology, Data curation. **Xiaoling Wang:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Frederic Mentink-Vigier:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmr.2025.107885.

Data availability

Data will be made available on request.

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